

Trace Metal Speciation: Equilibrium and Kinetic Considerations on Biological Effects, Phytoplankton Uptake and Sorption Processes in Coastal Waters (Field and Laboratory Studies)

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LONG-TERM GOALS

The long-term goals of our research are to:

- 1) Continue to develop and evaluate highly sensitive analytical techniques for determining the concentrations of bioactive trace metals in seawater and the extent of their complexation or chelation by natural organic ligands.
- 2) Conduct field and laboratory studies linking the marine chemistries of a suite of potentially toxic trace metals (Cu and Zn, along with Ni, Cd and Pb) of interest to the Navy, together with biologically essential metals (Mn and Fe) and interacting major nutrients (N, P and Si).

The central premises of the studies are that

- a) chemical speciation controls the reactivity of these trace metals, and
- b) understanding the exchange kinetics between the different chemical species or forms is essential to modeling the environmental fate and effects of these metals.

OBJECTIVES

The environmental fate and biotic effects of contaminant trace metals in coastal bays, harbors and estuaries is a priority research concern for the United States Navy. We are carrying out field and laboratory studies to address these issues. The studies entail determining the chemical speciation (or equilibrium partitioning between different chemical forms) of potentially toxic trace metals, in particular Cu and Zn (but also Cd, Pb and Ni). Our studies emphasize the role of strong metal-binding ligands in controlling the speciation and toxicity of these trace metals. In addition, we are carrying out studies to determine the kinetics of exchange between the various forms of the metals of interest. Of particular importance are the exchange kinetics with strong, metal-binding, dissolved organic ligands of both natural and anthropogenic origin, and between the solution species and binding sites associated with resuspended sediments. Our studies have two major components:

- 1) Determining the equilibrium partitioning between different chemical forms of trace metals.
- 2) Determining the kinetics of exchange between these various forms of trace metals.

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APPROACH

We have taken a multi-technique approach to our studies of dissolved metal concentrations and speciation. Over the years, we have developed many of the analytical techniques ourselves. The techniques include:

- 1) Chelation/solvent extraction/graphite furnace atomic absorption spectroscopy (GFAAS) for the determination of total dissolved metal concentrations.
- 2) Chelation/solid phase extraction/high resolution inductively coupled plasma mass spectrometry (ICP-MS) for the determination of total dissolved metal concentrations.
- 3) Anodic stripping voltammetry (ASV) at a thin mercury film (TMF), rotating glassy carbon disk electrode (RGCD) for speciation studies of Cu, Zn, Cd and Pb.
- 4) Competitive ligand equilibration (CLE) coupled with adsorptive cathodic stripping voltammetry (ACSV) for speciation studies of Fe, Ni, Cu, and Zn.
- 5) Cathodic stripping voltammetry (CSV) for the determination of the concentration and speciation of Mn.
- 6) Selective leaches of particulate trace metals followed by high resolution ICP-MS for a suite of trace metals and their various stable isotopes.
- 7) The use of low-abundance stable isotopes, together with high resolution ICP-MS, as tracers in kinetic studies.

We have applied these various analytical methods in a series of field studies to determine the partitioning of trace metals among their various physico-chemical forms, and provide basic thermodynamic data needed to predict the environmental fate and effects of these metals. Such field data are sorely lacking, particularly in estuarine and coastal areas influenced by marine, terrigenous and anthropogenic inputs. The major field efforts of this study have been in Narragansett Bay, Rhode Island, and in the South San Francisco Bay. Both of these sites have substantial anthropogenic inputs of trace metals, but differ in that they have either a relatively permanent phytoplankton bloom (upper parts of Narragansett Bay) or a pronounced spring phytoplankton bloom (South San Francisco Bay).

WORK COMPLETED

Our tasks completed this past year include:

- 1) A series of papers on our Narragansett Bay studies:
 - a) "Chemical speciation of dissolved Cu, Zn, Cd and Pb in Narragansett Bay, RI." 1998. *Marine Chemistry*, 60: 267-282 (Kozelka and Bruland).
 - b) "The complexation of 'dissolved' Cu, Zn, Cd and Pb by soluble and colloidal organic matter in Narragansett Bay, RI." 1998. *Marine Chemistry*, 62: 203-218 (Wells, Kozelka and Bruland).
 - c) "The distribution of colloidal and particulate bioactive metals in Narragansett Bay, RI." 1999. *Marine Chemistry*, in press (Wells, Smith and Bruland).
- 2) Two methods or intercomparison papers:
 - a) "An improved method for rapid preconcentration and determination of bioactive trace metals in seawater using solid phase extraction and high resolution inductively coupled mass spectrometry." 1999. *Marine Chemistry*, 63: 145-153 (Wells and Bruland).
 - b) "An intercomparison of voltammetric techniques to determine the chemical speciation of dissolved copper in a coastal seawater sample. *Analytica Chimica Acta*, in press (Bruland, Rue, Donat, Skrabal, and Moffett).
- 3) Two manuscripts dealing with

- a) "The biogeochemical cycling of manganese in San Francisco Bay: temporal and spatial variations in surface water concentrations." submitted - under review. (Roitz, Flegal and Bruland).
 - b) "Diel biogeochemical cycling in a hyperventilating estuarine environment." 1999. Estuaries, in press (Beck and Bruland).
- 4) A series of manuscripts (primarily funded by the NSF) on coastal upwelling regimes:
- a) "Iron-limited diatom growth and Si:N uptake in a coastal upwelling regime." 1998. Nature, 393: 561-564 (Hutchins and Bruland).
 - b) "An iron limitation mosaic in the California upwelling regime. 1998. Limnology and Oceanography, 43: 1037-1054 (Hutchins, DiTullio, Zhang and Bruland).
 - c) "Inducing phytoplankton iron limitation in iron replete coastal waters with a strong chelating ligand." 1999. Limnology and Oceanography, 44: 1009-1018 (Hutchins, Frank, Brzezinski and Bruland).
 - d) "Zinc and iron limited silicic acid and nitrate uptake in a coastal upwelling system." 1999. Marine Ecology Progress Series, in press (Franck, Brzezinski, Hutchins and Bruland).
- 5) Laboratory studies on the novel use of low abundance stable isotopes to trace adsorption/desorption equilibrium and kinetic partitioning of Cu, Zn and Ni with natural seawater and particles from South San Francisco Bay. A manuscript on this research is in preparation (A. Gee and K.W. Bruland).

RESULTS

In order to model the behavior and effects of trace metals in coastal waters, it is essential to quantify their solution speciation *in situ* and characterize the major biological, chemical and geological processes that influence their chemical speciation. We have developed a variety of analytical approaches that allow us to examine the speciation of a suite of potentially toxic metals (Cu, Zn, Cd, Pb, and Ni), along with the bio-active trace metals Mn and Fe, within the water column of estuarine and coastal environments. The importance of organic complexation in influencing the speciation and behavior of these trace metals is being recognized. We are also gaining insight into the kinetics of exchange between solution phases and suspended particles. Our field and laboratory studies are providing data from coastal waters on basic equilibrium and kinetic parameters that will serve as input and field validation of modeling efforts.

IMPACT/APPLICATIONS

The chemical speciation or form of trace metals in estuarine and coastal waters is the critical parameter governing their fate, bio-accumulation and toxicity to aquatic micro-organisms. The measurement of total dissolved concentrations of potentially toxic trace metals tells us very little about metal toxicity in coastal ecosystems. In order to understand and model the behavior and effects of trace metals in coastal waters it is essential to quantify their solution speciation *in situ* and characterize the major processes that influence their chemical speciation. There are field data indicating many bio-active trace metals exist predominantly as organic complexes or chelates in coastal waters. It appears that low concentrations of relatively strong and metal specific organic ligands play an important role in the chemical speciation of metals such as Cu and Zn. The bulk of these metal chelates appear to be relatively low molecular weight (less than 1000 Daltons NMW) and appear to be anionic and hydrophilic in character. Speciation studies carried out in coastal waters with dissolved Cu generally show that greater than 99% of the Cu is strongly bound or chelated with organic ligands. These studies also show that the concentration of free Cu²⁺ in coastal waters is usually found to be less than

10^{-11} M — a concentration that is non-toxic to most phytoplankton. There are cases, however, such as in the South San Francisco Bay where only ~80% of the Cu is chelated with these organic ligands. In these cases the free Cu^{2+} approaches 10^{-9} M and can be toxic to many phytoplankton species. However, in many coastal waters, higher concentrations of total dissolved Cu can be present yet be largely non-toxic if sufficiently high levels of natural organic chelators are present. Therefore, assessing the environmental impact of elevated trace metals in coastal systems is critically dependent on understanding the chemical speciation of these metals.

A mode of Cu toxicity to phytoplankton is that free Cu^{2+} can compete with the uptake and metabolism of nutrient metal ions such as Mn^{2+} and Zn^{2+} . Elevated concentrations of Mn^{2+} and Zn^{2+} can alleviate the toxic effects of free Cu^{2+} . A rigorous evaluation of the potential toxicity of Cu in coastal ecosystems needs to take Cu:Mn (or Cu:Zn) antagonisms into account.

TRANSITIONS

In the past year, the PI attended and actively participated in a series of meetings and workshops on water quality and impairment assessment on South San Francisco Bay. This is an example of attempts at making our research results and expertise available to a broader group of users.

RELATED PROJECTS

We have a number of collaborations with various groups. We have had an ongoing collaborative effort with Mark Wells (formerly at UCSC and now at the University of Maine) in studying the role of trace metals associated with colloids and particles in the marine environment. This has been a fruitful collaboration and has now yielded a series of papers. Second, we have had an informal collaboration with Bill Sunda where our field efforts have complemented his laboratory studies. Third, we have been involved in inter-comparison studies of our methods with various groups within the Harbor Processes program. Our research group and those of John Donat and Jim Moffett have all analyzed a common sample for copper speciation. The results of this inter-comparison study are in press in *Analytica Chimica Acta*. Finally, our ONR funded research closely complements our NSF funded research (The interdependence of the chemistry of Fe and Zn and phytoplankton dynamics in coastal upwelling regimes) and overlaps in coastal upwelling regimes off central California influenced by the San Francisco Bay.

PUBLICATIONS

Beck, N. and K.W. Bruland (1999). Diel biogeochemical cycling in a hyperventilating estuarine environment. *Estuaries*, in press.

Bruland, K.W., E.L. Rue, J.R. Donat, S. Skrabal, and J. Moffett (submitted). An Intercomparison of Voltammetric Approaches to Determine the Chemical Speciation of Dissolved copper in a coastal seawater sample (1999). *Analytica Chimica Acta*, in press.

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Hutchins D., J. DiTullio, Zhang and K.W. Bruland (1998). An iron limitation mosaic in the California Current upwelling regime. *Limnology and Oceanography*, 43: 1037-1054.

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Kozelka, P.B. and K.W. Bruland (1998). Chemical speciation of dissolved Cu, Zn, Cd and Pb in Narragansett Bay, RI. *Marine Chemistry*, 60: 267-282.

Roitz, J.S., A.R. Flegal and K.W. Bruland (submitted). The biogeochemical cycling of manganese in San Francisco Bay: temporal and spatial variations in surface water concentrations. *Estuarine, coastal and shelf Science*, submitted.

Wells, M.L., P.B. Kozelka and K.W. Bruland (1998). The complexation of 'dissolved' Cu, Zn, Cd and Pb by soluble and colloidal organic matter in Narragansett Bay, RI. *Marine Chemistry*, 62: 203-218.

Wells, M.L. and K.W. Bruland (1998). An improved method for rapid preconcentration and determination of bioactive trace metals in seawater using solid phase extraction and high resolution inductively coupled mass spectrometry. *Marine Chemistry*, 63: 145-153.

Wells, M.L., G.L. Smith and K.W. Bruland (1999). The distribution of colloidal and particulate bioactive metals in Narragansett Bay, RI. *Marine Chemistry*, in press.